

Application Note

Sulfur Dioxide Scrubber: pH Control

Industry: Refining, Food and beverage, Power, Oil and Gas, Pulp and Paper, Chemical
Product: pH/ORP Process Liquid Analyzers

Introduction

Power plant boiler houses designed to burn coal or high sulfur oil are required by Federal and State pollution regulations to “scrub” (remove) sulfur dioxide from flue gasses to meet emission limits. SO₂ in flue gasses is known to be harmful to the environment, as it is one contributor to the formation of acid rain. pH control is critical for the proper functioning of the scrubber system. Flue gas desulfurization (FGD) technology, is commonly referred to as a scrubber, is proved and effective method for removing sulfur dioxide (SO₂) emissions from the exhaust of coal-fired power plants.

Scrubber System

The basic principle of a sulfur dioxide scrubber system is the removal of SO₂ by using its chemical characteristics to combine with water. In some cases, parallel rotating rods create a series of short throat Venturi openings. A series of low pressure, large orifice spray nozzles direct the scrubbing solution into the system. “Scrubbing liquor” is introduced into the

system with the flue gas stream. Depending on the design of the scrubber, the gas can flow either concurrent (with) or counter-current (against) the scrubbing liquor. The high velocity turbulence caused by the Venturi openings ensures maximum gas to liquid contact. It is here that the droplets absorb the SO₂ as well as impacting and dropping particulates out of the stream. The scrubbed gas is then sent through a demister or re-heater to prevent condensation and exhausted to atmosphere.

The scrubbing liquor can be bubbled through a slurry or either lime, Ca(OH)₂, or limestone, CaCO₃ and water. Either lime or limestone will combine with the sulfite ions from the flue gas to form gypsum, CaSO₃. The SO₂ that is captured in a scrubber combines with the lime or limestone to form a number of byproducts. A primary byproduct is calcium sulfate, commonly known as gypsum. Spent scrubbing liquids are sent to clarifier where the insoluble gypsum is removed and the water is returned to the scrubber system.

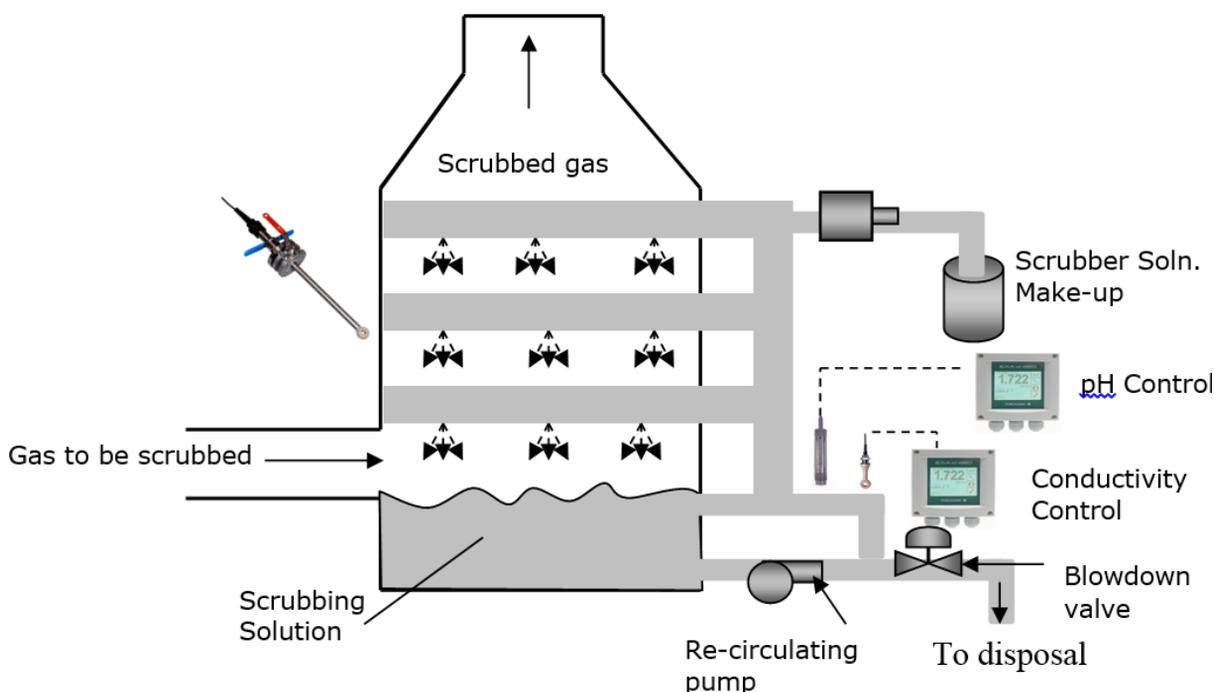


Figure 1.

The addition of lime or limestone to scrubbing solution is controlled by monitoring the pH of the solution. Lime slurries are generally alkaline with a control point near a pH of 12 while limestone slurries are more neutral.

pH Control

A pH measurement is one of the testing methods used to monitor continuous blowdown and replenishment. The SO₂ within the scrubbing gases can be controlled by maintaining the level of caustic scrubbing chemicals that are commonly used. pH is a critical factor for proper operation of a scrubber. It is also difficult to measure due to 2-15% solids and tendencies towards scaling, coating and plugging.

CaSO₄ concentration decreases slightly as pH decreases. Furthermore, because the concentration of oxygen dissolved in the slurry is constant, the formation of sulfate depends only on the concentration of SO₃. The precipitation of CaSO₄ increases as pH decreases, thus CaSO₄ is apt to form scale at a lower pH. Hard scale formation can be controlled by keeping the pH high.

The solubility of CaSO₃ increases greatly as pH decreases or conversely CaSO₃ forms a precipitate as pH increases. If pH is too high, "soft pluggage" occurs. Soft pluggage is due to formation of calcium sulfite precipitates which appear as large leaf like masses. Obviously maintenance of equipment that has soft pluggage is easier than with equipment that has hard scale. In many cases where soft pluggage has occurred, it can be melted off simply by lowering the pH (increasing solubility).

It is obvious that a potential dilemma exists, operation at too low pH promotes the formation of hard scale and operation at too high of a pH promotes the formation of soft pluggage. Only through experience can the proper pH range be determined. Typically limestone is added to achieve the desired level of SO₂ removal based on the sulfur content of the coal, the boiler load and the monitored SO₂ concentration of the flue gas, while maintaining the pH in the reaction tank at 5.5 to 6.0 pH. The pH sensor can be located in the re-circulating tank or the re-circulating line.

Conductivity Control

Conductivity is one of the most common testing methods used to monitor the concentration of scrubbing chemicals and by-products. As the concentration of the scrubbing chemical is depleted, its contribution to the total conductivity value will also decrease. However, occurring at the same time, the contribution to conductivity from the by-products is increasing. Therefore, a measurable decrease in conductivity is detected as the scrubbing solution is depleted.

Difficulties can arise, however, when more than one gas is being scrubbed. Depending upon the relative proportions of the gases, the by-products formed will differ, leading to variations in the conductivity background. Although a conductivity measurement can be difficult or impossible, it may still provide a useful alarm point to alert the operator to check a grab sample. In scrubbers where the scrubbing chemical concentration is maintained by continual replenishment and blowdown, conductivity can be used to initiate blowdown to prevent high dissolved solids build-up.

In continual replacement scrubbers, conductivity can be used to initiate blowdown to prevent high dissolved solids build up. Torodial or Inductive conductivity is the best form of measurement to use in this application and the sensor should be located where it will be exposed to a representative sample.

Product Recommendations

pH Measurement System

Process Liquid Analyzer:

- 2-wire FLEXA pH/ORP Analyzer
- 4-wire PH450G pH/ORP Analyzer

Sensor Selection:

Option #1: FU20/FU24 4 in 1 pH/ORP electrode
Alternatively, SENCOM sensor can be used. (FU20F/FU24F)

Option #2: FF20 Flow-thru assembly with individual measure, reference and temperature electrodes

i.e. SC21C-AGC55 and SM60-T1

Option #3: PR10 Retractable with FU20 or SC25V pH electrode

Option #4: PH8EFP pH electrode with PH8HS3 holder with automatic cleaning

Conductivity Measurement System

Process Liquid Analyzer:

- 2-wire FLEXA Inductive Conductivity Analyzer
- 4-wire ISC450G Inductive Conductivity Analyzer

Sensor Selection:

ISC40 Inductivity Conductivity electrode with various installation options available (insertion, flow through, retractable)

Note: For additional information on this application contact the local Yokogawa Process Liquid Analyzer Department